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Melt-infiltrated fibre-reinforced composite ceramic

The invention relates to a melt-infiltrated fibre-reinforced composite ceramic containing high-temperature-resistant fibres, in particular fibres based on Si/C/B/N, which are reaction-bonded to a matrix based on Si and containing at least one addition of another material, and also to a process for producing such a composite ceramic.

Such a process and such a composite ceramic are known from US-A-5 464 655.

Carbon fibre-reinforced carbon (C/C, also known as CFRC or in German language usage as CFC) is the first industrially successful development in the group consisting of fibre-reinforced composite ceramic materials.

Recently developed high-performance brake systems based on CFRC brake discs with specially developed friction linings, as are used, for instance, in motor racing, can only be produced using numerous impregnation or carbonization and graphitization cycles, so that the production process is extremely time-consuming, energy-intensive and costly and can take a number of weeks or months. In addition, CFRC brake discs have totally unsatisfactory braking properties for use in production vehicles which are not subjected to demanding operating conditions in the presence of moisture and at low temperatures. This manifests itself, inter alia, in decidedly non-constant coefficients of friction as a function of the operating temperature and the surface lining which makes regulation, as has hitherto been customary in 4-channel ABS systems, extraordinarily difficult or even impossible. In view of this background, attempts are being made to develop improved fibre-reinforced composite ceramic materials which can be used, for

example, as brake discs for high-performance brake systems in motor vehicles or in railway vehicles. Furthermore, such fibre-reinforced composite ceramic materials are also of interest for numerous other applications, for instance as turbine materials or as materials for sliding bearings.

Although silicon-infiltrated reaction-bonded silicon carbide (SiSiC) containing from 2 to 15% by mass of free silicon has been known since the 1960s and has also been introduced commercially for some applications in heat engineering. Problems in respect of internal stresses (internal stress due to cooling) occur in the manufacture of large and thick-walled components because of a step increase in the volume of the semimetallic silicon when it solidifies in the microstructure of the material. The stressing of the solidified silicon manifests itself, in many cases, in the formation of microcracks and in a reduction in adhesion at internal interfaces, so that the strength of the material is reduced and critical crack propagation under cyclic thermal and mechanical stress can be expected, particularly during prolonged use. In manufacture, the volume expansion on solidification leads to difficulties as have long been known when, for instance, water freezes in closed line systems, i.e. to rupture and breaking of the components and thus to high reject rates. In addition, the manufacture of SiSiC materials is relatively complicated and expensive.

US 5 079 195 A discloses a process in which a carbon-containing precursor body is infiltrated with a silicon melt which is alloyed with at least one element which is essentially insoluble in silicon and which forms high-melting phases, namely molybdenum, tungsten, rhenium, hafnium, zirconium, chromium, boron and titanium. In this way, only a minimum of free silicon remains in the composite body. As a result, the risk of crack formation in the material is reduced and the heat resistance is increased, so that the material is more mechani-

cally and thermally stabl .

EP 0 798 280 A2 discloses a composite c ramic material which is resistant to high temperatures and contains silicon carbide and molybdenum silicide.

However, a problem here is that these additives are expensive and therefore unsuitable for mass production. Furthermore, these additives are unsuitable for use of the ceramic as brake disc material, since the friction pairing with customary brake linings is adversely affected.

It is therefore an object of the present invention to provide an improved fibre-reinforced composite ceramic containing high-temperature-resistant fibres and also a process for producing such a composite ceramic, which makes possible very simple and inexpensive production of mass-produced components such as brake discs, with high thermal stability and hot strength together with sufficient oxidation resistance and thermal shock resistance being prerequisites.

The object of the invention is achieved by, in a melt-infiltrated fibre-reinforced composite ceramic of the type described at the outset, the matrix containing additions of iron.

The object of the invention is completely achieved in this manner. According to the invention, it has been recognized that this measure makes it possible, in a particularly inexpensive and environmentally friendly manner, to avoid the volume increase which occurs in the case of pure silicon and the additions of iron at the same time lead to improved braking performance in an application as a brake disc, since an improved friction pairing is obtained with conventional brake linings which are matched to brake discs based on grey cast iron. Brake systems based on such brake discs are thus more readily regulated since, in addition, they are less moisture-sensitive and are insensitive to low temperatures. Furthermore, there are no critical contact pressures which have an advers effect on regulatability,

as in the case of CFRC brake discs. In addition, the production process is simplified and made cheaper by the lowering of the melting point of the silicon melt by the addition of iron.

The alloying of the silicon melt used for melt infiltration with iron enables the step increase in volume on solidification of a pure silicon melt to be reduced or even largely avoided. In this way, the problems caused by the stressing of the solidified silicon are avoided, a higher strength, particularly with regard to cyclic thermal and mechanical stress, is achieved and at the same time the production process is simpler and less costly.

In an advantageous embodiment of the invention, preference is given to adding further additions of chromium, titanium, aluminium, nickel or molybdenum in a suitable ratio as passive layer formers to a matrix based on Si which contains additions of iron. These additives can effect the formation of protective passive layers, so that the oxidation and corrosion resistance is improved. In this case, different coefficients of thermal expansion of the alloying components lead to stress states in the matrix which compensate for the stresses caused by the fibres on cooling.

It is thus possible, according to the invention, to obtain a reaction-bonded, melt-infiltrated SiC ceramic (RB-SiC) in which the brittle Si as is present in hitherto customary RB-SiC ceramics is replaced by a phase enriched with Fe or Fe together with Cr and/or Ti, Mo, Ni or Al, which leads to a significant increase in strength and ductility of the ceramic.

In a further embodiment of the invention, the matrix is produced from a silicon alloy containing from 0.5 to 80% by weight of iron, preferably from about 5 to 50% by weight (based on the total mass of the alloy). Since ferrosilicon in comparatively pure form is used on an industrial scale in steel production, with grades having the compositions Fe25Si75 and Fe35Si65 being

commercially available, a considerable reduction in the raw material costs compared with the use of pure silicon is achieved. Furthermore, there is a lowering of the melting point from about 1410°C for pure silicon to about 1340°C when Fe25Si75 is used and to about 1275°C when Fe35Si65 is used.

In an additional embodiment of the invention, an additional 5-30% by weight of chromium, preferably about 7-12% by weight of chromium, based on the iron content, is added to the silicon melt which is used for melt infiltration.

This change to a three-material system consisting of Si-Fe-Cr enables the iron-containing phases of the composite ceramic to be protected against corrosion and at the same time allows the melting point to be lowered to less than 1400°C. For this purpose, it is useful to add at least about 7% by weight of chromium (based on the iron content), since from about 7 to 8% by weight of chromium is necessary to effect the formation of a passive layer of chromium(III) oxide, as is known from stainless steels. (Based on the total mass of the alloy, the proportion by weight of chromium is preferably from about 1 to 30% by weight, preferably from about 1 to 10% by weight.) However, for cost reasons it is preferable to select a chromium content which is not unnecessarily high. Although the corresponding metallic starting materials in the form of chromium-containing alloys (e.g. FeCr) are slightly more expensive than iron silicides such as FeSi ir $FeSi_2$, they give considerable advantages as a result of the improved oxidation resistance.

Fibres which are suitable for the fibre reinforcement include numerous high-temperature-resistant fibres, in particular fibres based on Si/C/B/N and having covalent bonds, with C fibres and SiC fibres being among the best known fibres which are suitable for the ceramics of the invention. In addition, use of, for instance, aluminium oxide fibres is also conceivable for particularly inexpensive products.

In an additional embodiment of the invention, the fibres are combined to form fibres bundles and are surface-impregnated.

In this way, commercially available rovings and multifilament strands (e.g. 12K bundles) can be used. These are advantageously impregnated on their surface, e.g. by means of pitch, to protect the fibre bundles against mechanical damage during production and to avoid excessive reaction and thus damage during the silicon infiltration by forming a carbon layer which can react to form SiC and thus protect the fibres.

In a further advantageous embodiment of the invention, the fibres are collected together to form short fibre bundles and can comprise, for example, C filaments having mean diameters of from about 5 to 12 μm and a length of from about 2 to 10 mm which are collected together to form fibre bundles containing from about 3000 to 14,000 filaments.

Such chopped carbon fibre bundles which are used for short-fibre reinforcement allow simplified production of a shaped body by pressing methods without costly lamination and post-impregnation having to be carried out. This makes possible inexpensive mass production and the parameters can be set so that virtually no shrinkage occurs and only minimal final machining, for example by grinding, of the finished components is necessary ("near net shape manufacture").

As regards the process, the object of the invention is achieved by a process for producing a fibre-reinforced composite ceramic containing high-temperature-resistant fibres, in particular fibres based on Si/C/B/N, which are reaction-bonded to a matrix based on Si, which comprises the following steps:

- production of a green body from fibres using binders and fillers by winding, lamination or pressing;

- pyrolysis of the green body under reduced pressure or protective gas in a temperature range from about 800°C to 1200°C to produce a porous shaped body;

- infiltration of the carbonized shaped body with a silicon melt which contains additions of iron.

As explained above, the volume increase which occurs when using pure silicon for the melt infiltration (about 10% by volume) can be considerably reduced or even avoided by means of such additions, so that a material having improved properties is obtained by a simplified and cheaper production process.

The internal stresses which occur in conventional fibre-reinforced, reaction-bonded SiC materials (RB-SiC) and lead to numerous reject parts during manufacture are reduced or largely avoided in this way. In a preferred embodiment of the invention, additions of iron and, if desired, of chromium, titanium, aluminium, nickel or molybdenum as passive layer former are mixed in suitable mixing ratios into the silicon melt.

Iron additions in the range from about 0.5 to 80% by weight of iron, preferably from about 5 to 50% by weight of iron, and, if desired, chromium additions of from 0.03 to 40% by weight of chromium, preferably from 1 to 30% by weight of chromium, in particular from about 2 to 10% by weight of chromium (based on the total mass of the alloy), give particularly